

---

(12) **UK Patent Application** (19) **GB** (11) **2 148 354 A**

(43) Application published 30 May 1985

---

(21) Application No 8425963

(22) Date of filing 15 Oct 1984

(30) Priority data

(31) 542600

(32) 17 Oct 1983

(33) US

---

(71) Applicant

W. R. Grace & Co. (USA-Connecticut),  
Grace Plaza, 1114 Avenue of the Americas, New York, New  
York 10036, United States of America

(72) Inventors

Peter Campbell Green,  
James Edson Jewell

(74) Agent and/or Address for Service

J. A. Kemp & Co.,  
14 South Square, Gray's Inn, London WC1R 5EU

(51) INT CL<sup>4</sup>

C09K 7/02

(52) Domestic classification

E1F GP

C3M 122 162 163 XX

(56) Documents cited

None

(58) Field of search

E1F

---

(54) Improved filtration reducer

(57) A water-based drilling fluid having improved water-loss properties contains water; an aluminum hydroxide viscosifying agent, of the formula  $\text{Al}(\text{OH})_3$ ; a primary water-loss reducer which is either cross-linked polyvinyl alcohol, cross-linked hydroxyalkyl cellulose or a mixture thereof; and a polyanionic cellulose as a further water-loss reducer. The preferred form of the polyanionic cellulose is sodium carboxymethyl cellulose having a molecular weight from about 100,000 to 1.2 million. The polyanionic cellulose is present in an amount up to 20% of the weight of the primary water-loss reducer. The drilling fluid can further contain a weighting agent such as barite. The composition is suitable for circulating in a bore hole while drilling the bore hole into subterranean formations.

GB 2 148 354 A

## SPECIFICATION

**Improved filtration reducer**5 1. *Field of the invention*

This invention relates to a drilling mud composition which has lower water-loss as measured by a reduced API filtration rate.

5

2. *Description of the previously published art*

10 One of the commercial type drilling muds used in oil-well and gas-well drilling is bentonite clay in water. To this bentonite clay drilling fluid can be added a water-loss inhibitor such as polyanionic cellulose. One of the problems with using just carboxymethyl cellulose as the water-loss inhibitor is that it is not effective in the presence of calcium chloride brines. When encountering brines having calcium ion concentrations over 1000 ppm, it has been recommended to remove the calcium ions by adding soda ash.

10

15 Recently, improved drilling fluids have been reported which contain alumina in the form of  $\text{AlO}(\text{OH})$  as the viscosifying agent and a crosslinked polyvinyl alcohol as a water-loss agent. These compositions are described in Block U.S. Patent No. 4,349,443 and they are shown to have superior rheological properties.

15

3. *Objects of the invention*

20 It is an object of this invention to further reduce the API filtration rate in a drilling fluid system containing alumina and a water-loss controller such as cross-linked polyvinyl alcohol or a cross-linked hydroxyalkyl cellulose without adversely affecting mud rheological properties.

20

It is a further object of this invention to prepare a drilling fluid which contains alumina in the form of  $\text{AlO}(\text{OH})$ , a water-loss controller such as cross-linked polyvinyl alcohol or a hydroxyalkyl cellulose and a

25 polyanionic cellulose which has a reduced API filtration rate.

25

It is a further object of this invention to prepare a water-loss reducer composition which is a combination of a primary water-loss reducer such as cross-linked polyvinyl alcohol or a cross-linked hydroxyalkyl cellulose and a polyanionic cellulose.

It is a further object of this invention to disclose a process of drilling a bore hole into a subterranean formation using a unique drilling fluid which reduces the API filtration rate.

30

*Summary of the invention*

A water-based drilling fluid has been formulated which has improved water-loss properties. The fluid contains water; an aluminum hydroxide viscosifying agent of the formula  $\text{AlO}(\text{OH})$ ; a primary water-loss reducer which is either cross-linked polyvinyl alcohol, cross-linked hydroxyalkyl cellulose or a mixture thereof; and a polyanionic cellulose as a further water-loss reducer. The preferred form of the polyanionic cellulose is sodium carboxymethyl cellulose having a molecular weight from about 100,000 to 1.2 million. The polyanionic cellulose is present in an amount up to 20% of the weight of the primary water-loss reducer. The drilling fluid can further contain a weighting agent such as barite. The composition is suitable for circulating in a bore hole while drilling the bore hole into subterranean formations.

35

40

*Description of the preferred embodiments*

To appreciate the significance of the present combination, a brief description of its history is helpful. In 1980 a new class of alumina viscosifiers for drilling muds were described by J. Block in U.S. Patent 4,240,915 based on alumina in the form of  $\text{AlO}(\text{OH})$ . At the time this new viscosifier was discovered one might have expected that it could be combined with any conventional water-loss controller such as polyanionic cellulose. Subsequent testing in the laboratory showed, however, that commercially available cellulose was not an effective component to use with this new alumina viscosifier. The data is presented infra in Comparison Example 1.

45

50 After further work with the new alumina viscosifier a very compatible water-loss controller was discovered in the form of a crosslinked polyvinyl alcohol and this composition is described by J. Block in U.S. Patent 4,349,443. Additional work found another water-loss controller in the form of a cross-linked hydroxyalkyl cellulose which is described by J. Block in U.S. Patent No. 4,366,070. The subject matter of these two patents is incorporated herein by reference.

50

55 Upon achieving these very successful drilling fluid mud compositions containing an alumina viscosifier in the form of  $\text{AlO}(\text{OH})$  and a water-loss controller in the form of either cross-linked polyvinyl alcohol or cross-linked hydroxyalkyl cellulose, there was no expectation that adding a polyanionic cellulose would be of any further help. Again, this was because the earlier laboratory tests had shown an adverse effect in rheological properties when the polyanionic cellulose was added to the alumina viscosifier.

55

60 When these drilling fluids are used in drilling their compositions are changed because they become contaminated with particles of drilled cuttings from the bore hole. It has now been unexpectedly discovered that it is possible to further reduce the API filtration rate of this working drilling fluid composition containing these cuttings by adding to the drilling fluid composition polyanionic cellulose.

60

The preferred aqueous drilling fluid mud composition contains  $\text{AlO}(\text{OH})$ , a primary water-loss reducer such as cross-linked polyvinyl alcohol or cross-linked hydroxyalkyl cellulose, and sodium carboxymethyl

65

cellulose. These components can be added to water to form a drilling fluid with a very low API filtration rate once the composition has been used in the well where it combines with the cuttings and clay from the bore hole formation.

While the theory of operation of this invention is not completely understood, the following may be helpful in comprehending the superior results obtained. The laboratory test composition described infra in Comparison Example 1 contained water, the AIO(OH) viscosifier and a small amount of Glen Rose Shale to simulate cuttings in a well. When some polyanionic cellulose was added to the test composition in the laboratory it is now believed the polyanionic cellulose interacted with the AIO(OH) to cause the poor rheological properties. However, when the present preferred composition is mixed with water and used as a working drilling fluid, it is believed the carboxymethyl cellulose interacts more with the cuttings from the bore hole than it does with the AIO(OH) so that there no longer is any adverse effect of the carboxymethyl cellulose on the AIO(OH) as occurred in the laboratory test composition. Furthermore, it is quite possible that the superior mixing and shearing action encountered in a field mud circulating system as compared to laboratory mixing contributes to this phenomenon. As is seen from the test data presented in the examples infra, there is a significant reduction in the API filtration rate by the addition of the carboxymethyl cellulose to the active working drilling mud system which contains cuttings and other materials from the bore hole formation.

Carboxymethyl cellulose is a commercially available material. One form that has been used is Driscose, sold by Drilling Specialties Co., which is a sodium carboxymethyl cellulose having a molecular weight of about 200,000. At this same molecular weight is CMC Regular grade sold by Drilling Mud, Inc. Also operable is a higher molecular weight carboxymethyl cellulose having a molecular weight of about 500,000 sold by Drilling Specialties Co. under the name Drispac. The operable molecular weight should range from 100,000 to 1.2 million. These molecular weights are measured by determining the degree of polymerization and then calculating the molecular weight based on the unit weight of the repeating unit. Other salt forms than the sodium salt form of carboxymethyl cellulose should also be operable.

When using the system of AIO(OH) and cross-linked polyvinyl alcohol, as the solids content of this drilling fluid increases (such as when the fluid is "weighted"), then it is permissible to use the higher molecular weight carboxymethyl cellulose.

The hydroxyl groups on the cellulose may be carboxymethylated to any desired extent; the extent of the reaction is referred to as degree of substitution, or DS. Since there are three hydroxyls per anhydroglucose unit, complete substitution is designated as a DS of 3. Carboxymethyl cellulose of quite low DS (approximately 0.2 to 0.3) is soluble in aqueous alkali. As the DS is increased, CMC becomes increasingly water-soluble. Commercial types of CMC are usually within the DS range of 0.50 to 1.0, but may vary from 0.4 to 1.5. Generally values of about .50 or higher are considered preferable.

The amount of the carboxymethyl cellulose employed can vary to whatever minimum small amount provides the added water loss reduction up to about 10 parts by weight carboxymethyl cellulose per 50 parts by weight of the primary water loss controller which can be either the cross-linked polyvinyl alcohol or the cross-linked hydroxyalkyl cellulose.

Although various types of viscosifying agents are known and used, it is preferred to employ a shear thinning liquid because this liquid will be easier to pump. In addition, such a liquid readily sweeps away the cuttings at the bottom of the hole and it then keeps them better in suspension as they are carried up to the top of the hole.

The fluids used according to the present invention have an n value of less than about 0.4 in the rheological power law model relationship of

$$\tau = K(\dot{\gamma})^n$$

where  $\tau$  represents the shear stress exerted on the aqueous system of the fluid in units such as pounds per 100 ft<sup>2</sup> or dynes/cm<sup>2</sup>;  $\dot{\gamma}$  is the shear rate in units of reciprocal time such as sec<sup>-1</sup>; K is a constant having the value of the shear stress of the particular system at shear rate of 1 sec<sup>-1</sup>; and n is a constant related to the degree of departure from Newtonian behaviour. For example, if n=1, the fluid is Newtonian, if n is less than 1, the fluid is shear-thinning. The lower the n value, the more shear-thinning the fluid.

One of the two solid component systems which can be used as a drilling fluid is the AIO(OH) - cross-linked polyvinyl alcohol system described in U.S. Patent No. 4,349,443 and in reissue application Serial No. 446,217 filed December 2, 1982, the entire contents of both are incorporated herein by reference. The amounts of the (a) AIO(OH) viscosifier and (b) cross-linked polyvinyl alcohol are sufficient to directly form an aqueous system having from 0.5 to 10 weight percent component (a) and from 0.3 to 5 weight percent of component (b). This mud system has also been described in the Oil and Gas Journal, January 11, 1982, page 79.

The AIO(OH) component used in all of the embodiments is preferably formed by mixing in an aqueous medium and under a high degree of agitation a water-soluble basic agent selected from the group consisting of an alkali metal aluminate, alkali metal hydroxide, ammonium hydroxide and mixtures thereof with a water-soluble acidic agent selected from an inorganic acid, aluminum chloride, aluminum sulfate, aluminum

nitrate, their hydrates and mixtures thereof; at least one of said basic and acidic agents being an aluminum containing compound: said acidic and basic agents being reacted in a ratio such that the resultant product imparts to said aqueous medium a pH of from at least about 8 to about 10.3

In the more preferred embodiment the concentration of the  $\text{AlO}(\text{OH})$  being made cannot be too high because the reaction mixture becomes too viscous. Similarly, the product  $\text{AlO}(\text{OH})$  concentration should not be too low because then the aluminum compound product is not being economically produced. Preferable  $\text{AlO}(\text{OH})$  concentrations in the reaction product mixture would be from about 1 to 6%.

Another preferred procedure for making the  $\text{AlO}(\text{OH})$  is to react  $\text{HCl}$  with a stabilized sodium aluminate solution as described in U.S. Patent No. (Application Serial No. 370,979 filed April 22, 1982), corresponding to British application No. 8309516 Serial No. 2120224. The method basically involves forming the  $\text{AlO}(\text{OH})$  in the presence of a hydroxy acid such as gluconic acid, tartaric acid, gallic acid, citric acid or a mixture of these acids or in the presence of a salt of these acids such as the sodium, potassium or ammonium salt.

The amount of the  $\text{AlO}(\text{OH})$  in the drilling fluid is broadly from about 0.5 to 10 weight percent. A more preferred range is from about 1-6%  $\text{AlO}(\text{OH})$  with 3%  $\text{AlO}(\text{OH})$  being most preferred.

The cross-linked polyvinyl alcohol component for this first embodiment is preferably a reaction product formed in an aqueous acidic medium having a pH of less than about 5.5 between polyvinyl alcohol having a weight average molecular weight of at least 20,000 with at least 0.01 percent of stoichiometry (i.e. one aldehyde group per 2 OH groups) of a compound containing at least one aldehyde group therein or capable of generating in situ at least one aldehyde group.

Conventionally polyvinyl alcohol is the hydrolyzed product of polyvinyl acetate. The hydrolysis should be at least about 75 percent complete and preferably from about 80 to 95 percent complete to form a suitable polyvinyl alcohol reactant. More preferably, the polyvinyl alcohol is about 87% hydrolyzed. Such a product is commercially available as Gelvatol 20-90 from Monsanto.

To lower the amount of the cross-linking compound containing the aldehyde group one can use a polyaldehyde which has more than one aldehyde group per molecule. A preferred polyaldehyde to form the desired polyvinyl alcohol/polyaldehyde reaction product is disclosed in U.S. Patent Application Serial No. 326,876 filed December 2, 1981, corresponding to British application No. 8233731, Serial No. 2110227. This polyaldehyde is an organic compound represented by the general formula:



35

wherein R is an organic radical capable of forming at least two covalent bonds with carbonyl groups. R can be selected from organic saturated or unsaturated aliphatic cycloaliphatic, aromatic or heterocyclic radicals, x is an integer of 0 or 1 and y is an integer of at least 2. The upper value of y is dependent on the capability of R to form covalent bonds with carbonyl groups. The preferred polyaldehydes are dialdehydes wherein R is a divalent hydrocarbon having from 1 to 12 carbons and preferably from 1 to 6 carbons, as for example, malonaldehyde, succinaldehyde, glutaraldehyde, adipaldehyde, malealdehyde, fumaraldehyde, phthalaldehyde and the like. The especially preferred material is glutaraldehyde. In addition, the dialdehyde having the above general formula wherein x is 0, which is known as glyoxal, is also a preferred material.

Another two solid component system which can also be used as a drilling fluid according to the present invention is the  $\text{AlO}(\text{OH})$  - cross-linked hydroxy  $\text{C}_1$ - $\text{C}_3$  alkyl cellulose system. This system is described in U.S. Patent 4,366,070 and the entire content of this patent is incorporated herein by reference. The amount of the  $\text{AlO}(\text{OH})$  and cross-linked hydroxyalkyl cellulose is substantially the same as for the corresponding  $\text{AlO}(\text{OH})$  - cross-linked polyvinyl alcohol system.

The cross-linked hydroxyalkyl cellulose component for this second embodiment is preferably a reaction product formed by contacting in an aqueous medium a hydroxy  $\text{C}_1$ - $\text{C}_3$  alkyl cellulose and from about 0.01 to 200 percent of stoichiometry based on the hydroxy groups of the cellulose of an agent capable of cross-linking the cellulose. The preferred hydroxyalkyl cellulose is hydroxyethyl cellulose. The agent is preferably epihalohydrin or either a compound having at least one aldehyde group therein or a compound capable of generating an aldehyde group in situ. The reaction between the hydroxyalkyl cellulose and epihalohydrin is carried out in an aqueous basic medium having a pH of about 9.5 or more. The reaction between the hydroxyalkyl cellulose and the compound having or capable of generating at least one aldehyde group therein is carried out in an aqueous acidic medium having a pH of about 5.5 or less.

It is also possible to use a combination of the cross-linked polyvinyl alcohol and the cross-linked hydroxyalkyl cellulose.

The amount of cross-linked polyvinyl alcohol or hydroxyalkyl cellulose is sufficient to directly form an aqueous system having from 0.3 to 5 weight percent of this material.

In another embodiment of the invention a chemical compound capable of converting to a higher oxidation state under alkaline conditions can be added to the fluid to provide a high temperature composition. This compound is described in U.S. Patent No. 4,389,319 and the entire contents of which are incorporated herein

by reference. The ability of the compound to make such a conversion is not meant to limit this embodiment to the requirement that the subject compound undergoes such conversion or that the agent, per se, is merely the precursor for the product required in the subject composition. The compound can be organic or inorganic and of monomeric, low molecular weight. Organic compounds which are suitable include

5 alkanols, preferably lower C<sub>1</sub>-C<sub>8</sub> alkanols, as for example, methanol, ethanol, n-propanol, iso-propanol, butanols and pentanols and the like; phenols such as phenol, C<sub>1</sub>-C<sub>3</sub> alkyl, aryl and alkaryl substituted phenols, tert-butylcatechol and hydroquinone and the like; mercaptans such as C<sub>1</sub>-C<sub>15</sub> alkanethiols and the like.

In addition the agent can be an inorganic readily oxidizable substance such as an alkali metal or alkaline earth metal or ammonium salt of sulfite, bisulfite, thiosulfate, hydrosulfite or nitrite; ferrous or cuprous metal salts of chloride or sulfate; and alkali metal borohydrides and the like and their equivalence. The preferred material are water soluble C<sub>1</sub>-C<sub>8</sub> alkanols, sulfite salts, bisulfite salts and nitrite salts of an alkali or alkaline earth metal or ammonium. The chemical compound capable of converting to a higher oxidation state described herein above should be used in amounts such that the ratio of the chemical compound to the

10 cross-linked polymeric reaction product is at least 0.2:1 with, preferably, a ratio of 0.2:1 to 1:1 and most preferably a ratio of at least 0.25:1 to 0.75:1.

Compositions having the combination of the above described components have unexpectedly been found to exhibit the desired combination of properties of pseudoplasticity and fluid-loss control which are unattainable by separate use of the materials. Further, the composition is capable of maintaining these

20 properties under elevated temperatures found in deep bore hole drilling such as greater than 250°F (121°C) and they are generally stable at temperatures of 300°F (149°C) and greater.

When drilling in wells which have higher down hole pressures, conventional weighting agents such as barite can be added to the drilling fluid as well as acid soluble weighting agents. Examples of acid soluble weighting agents include iron carbonates such as siderite, iron oxides including mixtures of different forms

25 of iron oxides, calcium carbonates and dolomite which is a calcium-magnesium carbonate. Also useable are other known weighting agents such as sodium chloride, calcium chloride, calcium bromide and zinc bromide. A preferred commercially available material is Densimix<sup>(R)</sup> Weight Material which is a micaceous hematite (an iron oxide of the formula Fe<sub>2</sub>O<sub>3</sub>) produced from the mineral itabirite and sold by Densimix, Inc., Houston, Texas.

30 Having described the basic aspects of our invention, the following examples are given to illustrate specific embodiments thereof.

#### *Tradenames of materials used*

Drispac is a form of carboxymethyl cellulose sold by Drilling Specialties Co. It has a molecular weight of

35 about 500,000.

Tergitol 15-S-3 is an antifoamer made by Union Carbide Corp. and it is a nonionic polyethylene glycol ether of linear alcohol.

Driscose is a form of carboxymethyl cellulose sold by Drilling Specialties Co. It has a molecular weight of about 200,000.

40 CMC Regular grade is a form of carboxymethyl cellulose sold by Drilling Mud, Inc. It has a molecular weight of about 200,000.

#### *Comparison Example 1*

This example illustrates the adverse rheological effect obtained when carboxymethyl cellulose is added to

45 the AIO(OH) viscosifier under laboratory test conditions.

A laboratory test aqueous mixture was made by adding to deionized water AIO(OH) in an amount of 3 wt.%, Glen Rose shale in an amount of 2.4 wt.% to simulate rock cuttings, and then Drispac in an amount of 1 wt.%. The resulting mixture was mixed for 20 minutes and it had a fluid loss of 20 ml, an n value of 0.53 and a K value of 7.8. This n value is high and not within the preferred value of n which is less than about 0.4 for this

50 system. The conclusion drawn is that CMC is the form of Drispac as a water-loss controller should not be used with the AIO(OH) viscosifier since the CMC adversely raises the n value.

#### *Examples 1-4*

These examples illustrate the preparation of working mud compositions which contain alumina, crosslinked polyvinyl alcohol as the primary water-loss reducer and cutting and clay particles from the bore hole formation to which various materials are added. For comparison purposes 1 gm per 350 ml is equivalent to 1 lb. per barrel. Their properties will be tested in Example 5.

Field mud from the suction pit of the Lundy 1-24 drilling operation located south of Elk City in Beckham County, Oklahoma was used. This field mud was initially made to contain about 4 lbs of AIO(OH) per barrel and about 5 lbs of crosslinked polyvinyl alcohol per barrel. During use, the polyvinyl alcohol concentration

60 and about 5 lbs of crosslinked polyvinyl alcohol per barrel. During use, the polyvinyl alcohol concentration was maintained, but the AIO(OH) concentration dropped down to the range of about 0.6-1 lb per barrel. The field mud weighed 9.2 pounds per gallon (1.1 kg/dm<sup>3</sup>), had a solids content of 6.2 percent and a pH of 9.5.

Example 1 serves as a control, where the field mud was used as received and it was given no further treatment.

65 Example 2 shows the effect of just adding an anti-foamer, Tergitol 15-S-3, in an amount of 8 drops per 350

ml of the field mud. These materials were mixed for 10 minutes at medium speed on a Hamilton Beach mixer.

Example 3 shows the further effect of adding sodium carboxymethyl cellulose in the form of 0.25 gm Driscose, sold by Drilling Specialties Co., to the composition of Example 2. Again, the materials were mixed for 10 minutes at medium speed on a Hamilton Beach mixer.

Example 4 shows the effect of adding another commercially available form of sodium carboxymethyl cellulose, CMC Regular grade having a molecular weight of about 200,000 sold by Drilling Mud, Inc. in the same amount of 0.25 gm to the composition of Example 2. Again, the materials were mixed for 10 minutes at medium speed on a Hamilton Beach mixer.

#### Example 5

This example illustrates the rheological properties of the materials obtained in Examples 1-4 and shows the reduction in the API filtration rate when adding carboxymethyl cellulose to the working mud system.

Each of the mixed samples made in Examples 1-4 was tested using the Baroid variable speed rheometer. The  $n$  and  $K$  values from the power law expression were determined. The API filtration rates were also determined. The results are set forth in Table 1.

TABLE 1

Dial Reading of Baroid Rheometer					
Example	1	2	3	4	
Composition	Control	Ex. 1 + anti-foamer	Ex. 2 + CMC	Ex. 2 + CMC	
speed (rpm)					
600	24	24	24	24	
300	17	17	16	17	
200	14	15	14	14	
100	11	12	10	11	
60	10	11	9	10	
35	9	10	8	9	
6	9	10	7	8	
10 sec. gel	6	5	4	4	
10 min. gel	12	11	9	9	
$n$	0.14	0.14	0.18	0.14	
$K$	5.6	6.0	4.3	5.6	
API Filtration, cc (a) not run	13.6	(a)	8.0	9.0	

From the results in Table 1, there is a significant decrease in the API Filtration rate from a value of 13.6 cc for the control to values from 8.0 to 9.0 when the sodium carboxymethyl cellulose was added. The sodium carboxymethyl cellulose did not significantly change the rheological properties since the  $n$  and  $K$  values remained at about the same acceptable levels.

#### Example 6

This example illustrates the rheological properties of the working drilling mud after it was aged about five months and when using a higher molecular weight form of carboxymethyl cellulose.

A 350 ml sample of the field mud of the type described in Example 1 was stored for about five months. Run A is a control where only 8 drops of Tergitol 15-S-3, an antifoamer, is added. In Run B the same 8 drops of Tergitol are added to 350 ml of the field mud along with 0.25 g. of Drispac, a carboxymethyl cellulose sold by Drilling Specialties Co. having a molecular weight of about 500,000. In both cases the mixtures were mixed for 10 minutes at medium speed on a Hamilton Beach mixer. Each of the mixtures was tested using a multispeed Fann 35 rheometer. The  $n$  and  $k$  values from the power law expression were determined. The API filtration rates were also determined. The results are set forth in Table 2.

TABLE 2

*Dial Reading of Baroid Rheometer*

5	<i>Example</i>	6A	6B	5
	<i>Composition</i>	<i>mud + antifoamer</i>	<i>Ex. 6A + CMC (Drispac)</i>	
10	<i>Speed (rpm)</i>			10
	600	37	27	
	300	26	18	
	200	20	14	
15	100	16	9	15
	60	14	7	
	30	12	5	
	6	8	2	
	10 sec. gel	5	2	
20	10 min. gel	18	10	20
	n	0.26	0.56	
	K	4.5	0.58	
	API Filtration, cc	10.4	9.2	

25 The results show a decrease in the API filtration rate when the higher molecular weight CMC is added. Unfortunately for this unweighted mud there is also an undesired increase in the n value, when using the CMC of molecular weight of 500,000.

30 *Example 7*

This example shows the lack of deterioration of the rheological properties when the higher molecular weight Drispac is added to a weighted field mud.

A weighted field mud which had been weighted with barite to a mud density of 14.7 pounds per gallon (1.76 kg/dm<sup>3</sup>) contained approximately 1.4 wt.% (4.9 lb. per barrel) crosslinked polyvinyl alcohol and 0.4 wt.% (1.4 lb per barrel) AlO(OH). In Example 7A the rheological properties are determined and then in Example 7B the properties are again measured after Drispac was added in an amount of 0.25 pounds per barrel of mud (0.25 g per 350 ml) and the mixture mixed on a Hamilton Beach mixer for 10 minutes. The fluid loss is determined in accordance with the American Petroleum Institute's procedure API No. RP-13B for both ambient and high temperature conditions. The TFL is the total fluid loss after 30 minutes. The HTHP value was obtained under the same API No. RP-13B procedure where the fluid was heated in a cell at 250°F (120°C) and the pressure applied was 500 psi (3450 kPa). The amount of fluid collected after 30 minutes was multiplied by 2 according to the test procedure. The results are set forth in Table 3.

TABLE 3

45	<i>Example 7</i>	7A	7B	45
	<i>Composition</i>	<i>weighted mud</i>	<i>7A + Drispac</i>	
50	n	0.1	0.18	50
	k	21.0	21.0	
	TFL(ml)	5.4	3.2	
	HTHP(ml)	68.0	30.4	

55 These results show that when there is a substantial amount of the weighting agent present in the drilling mud, the addition of the higher molecular weight Drispac reduces the filtration loss and it does not significantly affect the rheology as measured by the n and k values.

## 60 CLAIMS

1. A water-based drilling fluid suitable for circulating in a bore hole while drilling the bore hole into subterranean formations comprising water; an aluminum hydroxide viscosifying agent; a primary water-loss reducer selected from the group consisting of cross-linked polyvinyl, cross-linked hydroxyalkyl cellulose and mixtures thereof; and a polyanionic cellulose as a further water-loss reducer.

2. The water-based drilling fluid according to claim 1, further comprising a weighting agent.
3. The water-based drilling fluid according to claim 1 or 2, wherein the viscosifying agent has the formula  $\text{AlO}(\text{OH})$ .
4. The water-based drilling fluid according to claim 1, 2 or 3, wherein the polyanionic cellulose has a  
5 molecular weight from about 100,000 to 1.2 million. 5
5. The water-based drilling fluid according to any one of claims 1 to 4 wherein the polyanionic cellulose is carboxymethyl cellulose.
6. The water-based drilling fluid according to claim 5, wherein the carboxymethyl cellulose is in the sodium salt form.
- 10 7. The water-based drilling fluid according to any one of claims 1 to 6 wherein the polyanionic cellulose is present in an amount up to 20% of the weight of said primary water-loss reducer. 10
8. The water-based drilling fluid according to claim 7, wherein the polyanionic cellulose is present in an amount of from 10 to 20% of the weight of the cross-linked polyvinyl alcohol.
9. The water-based drilling fluid according to any one of claims 1 to 8, wherein said primary water-loss  
15 reducer is cross-linked polyvinyl alcohol. 15
10. The water-based drilling fluid according to claim 1 substantially as hereinbefore described.
11. A water-loss reducer composition for use in a water-based drilling composition comprising a primary water-loss reducer selected from the group consisting of a cross-linked polyvinyl alcohol, a cross-linked hydroxyalkyl cellulose and mixtures thereof and a polyanionic cellulose having a molecular weight of from  
20 about 100,000 to 1.2 million in an amount up to 20% by weight based on the weight of said primary water-loss reducer. 20
12. A water-loss reducer composition according to claim 11, wherein said primary water-loss reducer is cross-linked polyvinyl alcohol.
13. A water-loss reducer composition according to claim 11 or 12, wherein said polyanionic cellulose is  
25 present in an amount of about 10-20% by weight based on the weight of said primary water-loss reducer. 25
14. A water-loss reducer composition according to claim 11, 12 or 13 wherein said polyanionic cellulose is sodium carboxymethyl cellulose.
15. A process of drilling a bore hole into a subterranean formation using conventional bore hole drilling equipment, which comprises circulating into the bore hole while drilling the drilling fluid of any one of claims  
30 1 to 10. 30